

EFFECTS OF DISPERSED Mo CATALYSTS AND H₂O ADDITION ON HYDROGENATION AND HYDROCRACKING OF 4-(1-NAPHTHYLMETHYL)BIBENZYL

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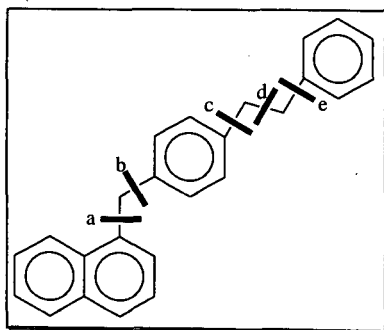
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This paper reports our results on the effects of dispersed Mo catalysts and H₂O addition on hydrogenation and C-C bond hydrocracking of 4-(1-naphthylmethyl)bibenzyl, abbreviated as NMBB. Batch studies in micro reactors (initial cold H₂ pressure of 6.9 MPa) revealed that active catalysts can be generated in situ from either ammonium tetrathiomolybdate (ATTM) or Mo(CO)₆ under the reaction conditions (350 or 400 °C, 30 min) with the main catalysis of the latter for NMBB hydrogenation, but the former for C-C bond cleavage. At 350 °C hydrocracking of NMBB proceeds with ATTM, with the bond cleavage occurring at the C-C bond between naphthyl and bibenzylmethyl groups to produce naphthalene and 4-methylbibenzyl. Runs at 350 °C using Mo(CO)₆ lead to tetrahydro-NMBB-derivatives and few cleavage products. Water added to Mo(CO)₆ suppressed hydrogenation. The combination Mo(CO)₆ and S lead to almost complete conversion of NMBB. A run with Mo(CO)₆/S/H₂O gave similar results. It appears that water can increase NMBB conversion with ATTM at 350 °C but decreases conversion for runs at 400 °C.

Keywords: Model reactions, hydrocracking, dispersed catalysts, Mo-based catalysts.

INTRODUCTION

Ever since Bergius (1) demonstrated the feasibility of dispersed coal liquefaction, numerous studies have been made to make the process more cost effective. Suitable catalytic systems contain Co, Ni, Mo or its combinations (2), either as inorganic complexes, or organometallic species in a concentration of 1 wt % or lower. Good solubility of catalyst precursors generally leads to better catalyst dispersion and greater effectiveness for liquefaction reactions (3). It has been demonstrated (4) that highly dispersed catalysts from organometallic precursors can be effective for hydrogenating the coal with molecular hydrogen without relying upon a donor solvent. One way to achieve better dispersion is the use of soluble organometallic precursors which produce in situ finely dispersed active catalyst particles at elevated temperatures. Greater catalyst surface area increases the yield of products dramatically, due to greater hydrogen activation by augmented reactive catalyst sites. The beneficial effect of S on conversion has been demonstrated (5) for a variety of transition metal-based catalysts. Recent research in our group (6) has demonstrated a strong synergistic effect between a Mo sulfide catalyst and water in low severity coal liquefaction reactions. This finding seems to be contrary to conventional wisdom. Under normal liquefaction conditions, water deactivates Mo-based catalysts (7). In order to help understand the mechanism of water promoted liquefaction reactions, we also examined the effect of water on the catalytic reactions of the model compound NMBB which represents a simplified model of coal. This paper reports our work on hydrocracking experiments of NMBB over different Mo-based metal catalyst precursors. The effects of Mo-based catalyst precursors on conversion and product selectivity, as well as the influence of the sulfur and water addition and reaction temperature on the product distribution will be discussed.



Scheme 1: Potential cleavage sites in 4-(1-naphthylmethyl)bibenzyl.

EXPERIMENTAL SECTION

Preparation of Catalyst Precursors

Sulfur and ammonium tetrathiomolybdate were purchased from Aldrich, Mo(CO)₆ from Alfa and the model compound NMBB from TCI America. GC-MS confirmed sufficient purity of NMBB

(>99 %) and it was used without further purification.

Model compound reactions

A reactor with a capacity of 33 mL was loaded with ca. 0.25 g NMBB, 1 wt % catalyst precursor (1 wt % Mo based on NMBB) and 0.14 g solvent (tridecane). When water was added, the molar ratio of H_2O to NMBB was 10, corresponding to a wt ratio of H_2O /NMBB of 0.56. The reactor was purged three times with H_2 and then pressurized with 6.9 MPa H_2 at room temperature for all experiments. A preheated fluidized sand bath was used as the heating source and the horizontal tubing bomb reactor was vertically agitated to provide mixing (about 240 strokes/min). After the reaction the hot tubing bomb was quenched in cold water. The liquid contents were washed with 15 ml $CHCl_3$ through a low speed filter paper for qualitative and quantitative GC analysis of the filtrate. All runs were carried out at least twice to confirm reproducibility. When sulfur was added, the atomic ratio of S:Mo was 4:1.

The products were identified by GC-MS using a Hewlett-Packard 5890 II GC coupled with a HP 5971A mass-selective detector operating at electron impact mode (EI, 70 eV). The column used for GC-MS was a J&W DB-17 column; 30-m X 0.25-mm, coated with 50 % phenyl 50 % methylpolysiloxane with a coating film thickness of 0.25 μm . For quantification, a HP 5890 II GC with flame ionization detector and the same type of column (DB-17) was used. Both GC and GC-MS were temperature programmed from 40 to 280 $^{\circ}C$ at a heating rate of 4 $^{\circ}C$ /min and a final holding time of 15 min. The response factors for 10 of the products were determined using pure compounds. More experimental details may be found elsewhere (8).

RESULTS AND DISCUSSION

NMBB Reaction at 350 $^{\circ}C$

Effect of Precursor Type and S Addition

Table 1 presents the results of non-catalytic and catalytic runs of NMBB with dispersed catalysts at 350 $^{\circ}C$. NMBB is essentially inert at 350 $^{\circ}C$ under H_2 pressure in a non-catalytic run. ATTM showed remarkable catalytic effect on NMBB conversion at 1 wt % Mo loading. The main products are 4-methylbibenzyl (4-MBB) and naphthalene, which were formed from cleavage of bond **a** in NMBB. It is clear that the molybdenum sulfide in situ generated from ATTM at 350 $^{\circ}C$ is catalytically active, and can promote the cleavage of C-C bond **a** in NMBB. ATTM decomposition also generates extra sulfur. However, our results in Table 1 shows that adding sulfur alone, or H_2O alone, had little effect on NMBB conversion.

The material in situ generated from $Mo(CO)_6$ at 350 $^{\circ}C$ acted as a hydrogenation catalyst. The dominant product with $Mo(CO)_6$ is tetrahydro-NMBB (TH-NMBB). Sulfur addition to $Mo(CO)_6$ increased NMBB conversion significantly, from 50.8 to 94.3 %. Adding sulfur also changed the product distribution pattern. The major products with $Mo(CO)_6 + S$ are 4-MBB and naphthalene arising from cleavage of bond **a**. The run with $Mo(CO)_6 + S$ also produced considerable amounts of bibenzyl and methylnaphthalene, probably via cleavage of bond **b** in NMBB.

Figure 1 compares the product distribution for runs at 350 $^{\circ}C$. An interesting result was found in the run with $Mo(CO)_6$ at 350 $^{\circ}C$. Most of the total conversion of 50.8 % can be attributed to the formation of TH-NMBB derivatives (45.5 mol %). This finding suggests that under low severity reaction conditions the initial step in hydrocracking of NMBB is the addition of hydrogen. Several TH-NMBB derivatives (MW 326) can be detected in the GC-MS analysis, indicating hydrogenation of different aromatic moieties in the model compound. At elevated temperatures activated $Mo(CO)_6$ cleaves NMBB completely; no more TH-NMBB derivatives can be detected, as described later.

Effect of H_2O Addition

The addition of H_2O to ATTM enhanced NMBB conversion and increased the yields of 4-MBB and naphthalene. Therefore, the co-use of ATTM and water appears to be beneficial for NMBB hydrocracking at 350 $^{\circ}C$. However, adding H_2O to $Mo(CO)_6$ decreased NMBB conversion to the level close to a non-catalytic run. This indicates that added H_2O either inhibited the formation of a catalytically active phase or passivated the active sites on the surface of the active phase, or reacted to form some kind of catalytically inactive material. However, adding H_2O to $Mo(CO)_6 + S$ system did not have significant effects on NMBB conversion or product distribution.

It is interesting to note that H_2O addition to the catalytic runs with either ATTM or $Mo(CO)_6 + S$ system did not alter the product distribution pattern, suggesting that the added water did not alter the reaction pathways in these cases.

NMBB Reaction at 400 $^{\circ}C$

Table 2 shows the results for non-catalytic and catalytic runs of NMBB at 400 $^{\circ}C$. NMBB is not very reactive in a non-catalytic run at 400 $^{\circ}C$ under H_2 pressure, as its conversion is below 4 %. Sulfur, however, began to show catalytic effect when the temperature is increased from 350 to 400 $^{\circ}C$.

Both ATTM and $Mo(CO)_6$ afforded higher conversion of NMBB at 400 $^{\circ}C$ than the corresponding runs at 350 $^{\circ}C$. ATTM alone is a more effective catalyst precursor than $Mo(CO)_6$ alone, in terms of higher NMBB conversion (93.0 vs. 79.6 %). Addition of water to ATTM in the run at 400 $^{\circ}C$, however, had negative impact on NMBB conversion. These results are consistent

with those for catalytic hydroliquefaction of coal, where H₂O addition had a strong promoting effect for runs at 350 °C, but inhibiting effect for runs at 400 °C (6).

It appears from our results that water has two opposing effects on NMBB conversion at 350 and 400 °C. Possibility exists that the ratio of water to catalyst is also influential. Farcașiu et al. (9) reported that NMBB cleavage at 420-430 °C with various dried iron oxide precursors were different from rehumidified catalysts. Addition of small quantities of water increases, to some extent, the catalytic activity. Completely rehumidified iron oxides showed very low catalytic activity compared to partially hydrated iron oxide. The activity of the system as an acidic catalyst is destroyed by larger amounts of water (longer rehumidification time).

Figure 2 further compares the product distribution for runs at 400 °C. For the runs with ATTM and ATTM+H₂O, 4-MBB and naphthalene are the major products. In the case of Mo(CO)₆, the yield of tetralin is higher than that of naphthalene. Apparently, the activity and selectivity of a dispersed Mo catalyst for NMBB hydrocracking depends on the catalyst precursor type and reaction conditions. Since it is the precursor that was charged into the reactor, an activation into catalyst is involved during the heat up and the subsequent reaction.

It is known (3,5,10) that the S-free catalyst precursors like metal carbonyls require the addition of sulfur for sufficient activity in coal liquefaction; activation of ATTM into the catalytically active species (close in composition to MoS₂) occurs at a temperature of ≥325-350 °C. This temperature range was used in our model reactions. Sulfur addition to Mo(CO)₆ generates MoS₂ after high temperature activation. The resulting product distribution at 350 °C is very similar to runs with ATTM (Table 1). We assume that the active catalytic species is similar to that from ATTM. Unlike ATTM, the organometallic complex Mo(CO)₆ decomposes at much lower temperatures. The active catalyst particles will be readily available under the conditions employed. This may rationalize why the NMBB conversion is higher with Mo(CO)₆ than with ATTM at 350 °C. However, for runs at 400 °C, the NMBB conversions with ATTM and Mo(CO)₆ are similar to each other (8).

With respect to the effect of the catalyst loading level, we have reported some results on NMBB hydrocracking over dispersed catalysts at 2.11 wt % metal loading (8). Decreasing Mo loading level from 2.11 wt % to 1 wt % (this work) did not have negative impacts on NMBB conversion with ATTM, but caused some changes in product distribution from NMBB with Mo(CO)₆.

CONCLUSIONS

Dispersed fine particles in situ generated from either water-soluble precursors such as ATTM or oil-soluble precursors such as Mo(CO)₆, can be effective Mo catalysts for promoting the cleavage of certain C-C bonds such as bond a in NMBB at 350-400 °C. When the sulfur-free precursor is used, adding sulfur helps to improve catalytic activity, particularly hydrocracking activity. When ATTM is used at low temperature (350 °C), adding water seems to be beneficial in improving NMBB conversion.

ACKNOWLEDGMENTS

We wish to thank Dr. H. Schobert for his encouragement and support. This project was supported by the U.S. Department of Energy, Pittsburgh Energy Technology Center under contract DE-AC22-92PC92122. We are grateful to Dr. U. Rao of PETC for his support. We also thank Mr. R. Copenhagen for the fabrication of reactors.

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Table 1: Effect of S and H₂O on hydrocracking of NMBB at 350 °C.

Experiment #	105	95	107-1/ 109-1	94/96/ 108/110	97	98	100	102
Catalyst Precursors*	S [1.4 wt %]	H ₂ O	ATTM	ATTM+ H ₂ O	Mo(CO) ₆	Mo(CO) ₆ + H ₂ O	Mo(CO) ₆ +S	Mo(CO) ₆ +S+H ₂ O
Products [mol %]								
Tetralin			6.6	8.0	3.5		20.6	13.5
Naphthalene	4.4	2.4	25.6	40.0	1.6	1.5	55.4	58.8
2-MTHN ^a				0.1			1.4	0.8
1-MTHN			0.4	0.6			1.7	1.1
2-Methylnaphthalene				0.16			1.9	1.4
1-Methylnaphthalene			1.7	2.9			5.7	5.8
Bibenzyl	0.2		4.7	6.5	0.5		21.2	15.8
4-Methylbibenzyl	3.7	1.9	33.2	50.2	3.8	1.1	74	71.1
TH-NMBB		1.6	5.8	5.3	45.5		2.1	3.1
Conversion [wt %]	4.1	3.7	42.4	60.0	50.8	1.3	94.3	88.2

^aMethyltetrahydronaphthalene. *when S was added, the atomic ratio S:Mo was 4:1.

Table 2: Effect of Mo-based catalyst precursors on hydrocracking reactions of NMBB at 400 °C.

Experiment #	21	78	91	92	106
Catalyst Precursors*	Non-catalytic run	S [1.2 wt %]	ATTM	ATTM+H ₂ O	Mo(CO) ₆
Products [mol %]					
Toluene	0.3	1.4	4.2	3.9	1.5
Tetralin	0.2	0.8	21.8	6.8	49.5
Naphthalene	0.6	24.8	58.1	42.9	10.5
2-MTHN ^a			0.7	0.6	1.2
1-MTHN			1.7	0.5	5.2
2-Methylnaphthalene			1.0	1.3	
1-Methylnaphthalene		1.7	6.8	5.6	0.9
Bibenzyl		2.4	14.5	11.1	12.7
4-Methylbibenzyl	1.3	22.1	77.3	53.1	58.5
Conversion [wt %]	3.9	26.1	93.0	63.2	79.6

^aMethyltetrahydronaphthalene, *when S was added, the atomic ratio S:Mo was 4:1.

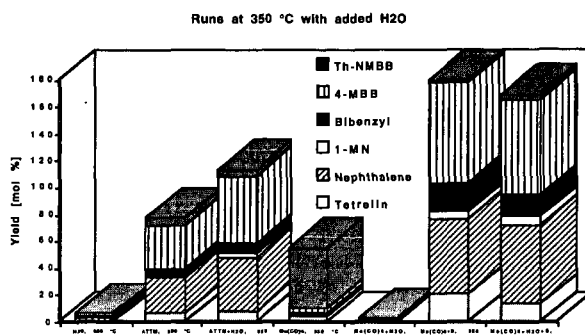


Figure 1. Effect of S and water on hydrocracking of NMBB.

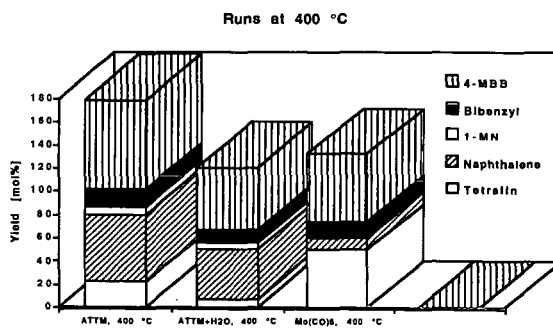


Figure 2: Effect of Mo-based catalysts on hydrocracking of NMBB.